

## PATENT ABSTRACTS OF JAPAN

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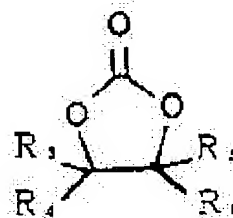
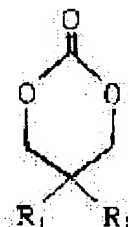
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## (54) NON AQUEOUS ELECTRICAL DOUBLE-LAYER CAPACITOR AND NON-AQUEOUS ELECTROLYTE THEREFOR

## (57)Abstract:

PROBLEM TO BE SOLVED: To improve breakdown voltage, safety, and charging/discharging cycle characteristics by an electrolyte solvent containing a specific annular carbon ester and an electrolyte.

SOLUTION: A non-aqueous electrolyte is constituted of cyclic carbon ester that is expressed by an expression 1 (R1 and R2 may be equal or different and an alkyl group with 1-4 carbons, a non-saturation carbon hydroxyl group with 2-4 carbons or aryl group with 6-12 carbons), an electrolyte solvent containing cyclic carbon ester that is expressed by an expression 2 (R3, R4, R5, and R6 may be equal or different and is alkyl group with 1-4 carbons or aryl group with 6-12 carbons), and an electrolyte. Also, R1-R6 as cyclic carbon ester being expressed by the expressions 1 and 2 are CH3 or C2H5.



## LEGAL STATUS

[Date of request for examination]

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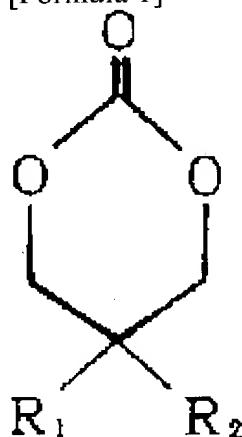
## CLAIMS

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[Claim(s)]

[Claim 1] Nonaqueous electrolyte for electric double layer capacitors characterized by consisting of an electrolyte solvent containing an annular carbonate expressed with the following type (I) or (II), and an electrolyte.

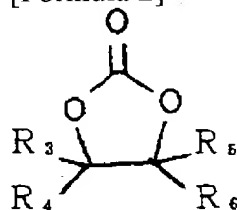
[Formula 1]



( I )

(Among a formula, even if R<sub>1</sub> and R<sub>2</sub> are the same, they may differ from each other, and they are the alkyl group of carbon numbers 1-4, the unsaturated hydrocarbon radical of carbon numbers 2-4, or the aryl group of carbon numbers 6-12.)

[Formula 2]



( II )

(Among a formula, even if R<sub>3</sub>, R<sub>4</sub>, R<sub>5</sub>, and R<sub>6</sub> are the same, they may differ from each other, and they are the alkyl group of carbon numbers 1-4, or the aryl group of carbon numbers 6-12.)

[Claim 2] Nonaqueous electrolyte for electric double layer capacitors according to claim 1 characterized by R<sub>1</sub>-R<sub>6</sub> of an annular carbonate which are expressed with said formula (I) or (II) being CH<sub>3</sub> or C<sub>2</sub>H<sub>5</sub>.

[Claim 3] Nonaqueous electrolyte for electric double layer capacitors according to claim 1 or 2 characterized by an electrolyte solvent being a mixed solvent of an annular carbonate expressed with a formula (I) and/or (II), and other carbonates.

[Claim 4] An electric double layer capacitor characterized by using nonaqueous electrolyte for electric double layer capacitors according to claim 1 to 3.

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[Translation done.]

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## DETAILED DESCRIPTION

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### [Detailed Description of the Invention]

[0001]

[Field of the Invention] Energy density of this invention is high in more detail about the nonaqueous electrolyte for electric double layer capacitors containing an annular carbonate, and it is related with the nonaqueous electrolyte which can offer the electric double layer capacitor excellent in withstand voltage and a charge-and-discharge cycle property.

[0002]

[Background of the Invention] Conventionally, the electric double layer capacitor with a middle capacity of a cell and a capacitor is widely used as DC power supply of small power as the backup power supply of IC or memory, and an object for assistance / alternative of a rechargeable battery. However, while new portable electronic equipment, such as a camcorder/movie, a cellular phone, and a laptop computer, appears one after another in recent years, in order to attain the further improvement in functional of such portable electronic equipment, high energy density-ization is demanded from the electric double layer capacitor used for uses, such as assistance, an alternative, etc. of a backup power supply and a rechargeable battery.

[0003] This electric double layer capacitor does not change a chemical change into electrical energy like a battery, uses capacity with the big electric double layer produced in the interface of an electrode and the electrolytic solution, and takes the charge of this double layer in and out like the charge and discharge of a cell. The configuration of such an electric double layer capacitor usually uses the corrosion resistance electrolytic solution, and it is arranged so that the electrode of two sheets fabricated with a material with big surface area like activated carbon and binders, such as a fluororesin, may counter through the porous separator made from polyethylene or polypropylene.

[0004] As the electrolytic solution of such an electric double layer capacitor, the aqueous solution system electrolytic solution and the organic solvent system electrolytic solution (nonaqueous electrolyte) are used. However, withstand voltage is low (about 1.2 V), and the aqueous solution system electrolytic solution had the problem that it was difficult to obtain the electric double layer capacitor of high energy density.

[0005] On the other hand, it is possible for the organic solvent system electrolytic solution (nonaqueous electrolyte) to obtain the capacitor of high energy density, since withstand voltage is high compared with the aqueous solution system electrolytic solution, and, for this reason, the electric double layer capacitor using nonaqueous electrolyte is beginning to spread quickly as a backup power supply of consumer electronics.

[0006] As such nonaqueous electrolyte, what mixed electrolytes, such as 4 fluoride way acid 4 ethylammonium, is used for non-aqueous solvents which are generally solvents of a high dielectric constant, such as propylene carbonate and gamma-butyrolactone.

[0007] However, in the above electrolytic solutions, since electrical conductivity was low, the internal resistance of a capacitor increased and there was a problem that the capacitor of high power was not obtained. Moreover, when future large high energy density-ization was made, the above-mentioned electrolytic solution of withstand voltage

may be inadequate, and an appearance of the nonaqueous electrolyte which was more excellent in the charge-and-discharge cycle property was desired.

[0008]

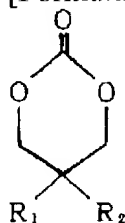
[Objects of the Invention] This invention aims at offering the nonaqueous electrolyte which is going to solve the trouble accompanying the above conventional technology, was excellent in withstand voltage and a charge-and-discharge cycle property, and was excellent in safety.

[0009]

[Summary of the Invention] The nonaqueous electrolyte for electric double layer capacitors concerning this invention is characterized by consisting of an electrolyte solvent containing the annular carbonate expressed with the following type (I) or (II), and an electrolyte.

[0010]

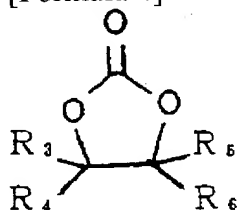
[Formula 3]



[0011] (Among a formula, even if R1 and R2 are the same, they may differ from each other, and they are the alkyl group of carbon numbers 1-4, the unsaturated hydrocarbon radical of carbon numbers 2-4, or the aryl group of carbon numbers 6-12.)

[0012]

[Formula 4]



[0013] (Among a formula, even if R3, R4, R5, and R6 are the same, they may differ from each other, and they are the alkyl group of carbon numbers 1-4, or the aryl group of carbon numbers 6-12.)

As for R1-R6 of an annular carbonate which are expressed with said formula (I) or (II), it is desirable that it is CH3 or C2H5.

[0014] Moreover, as for the above-mentioned electrolyte solvent, it is desirable that it is the mixed solvent of the annular carbonate expressed with a formula (I) and/or (II) and other carbonates. The electric double layer capacitor concerning this invention is characterized by using the above-mentioned nonaqueous electrolyte for electric double layer capacitors.

[0015]

[Detailed Description of the Invention] Hereafter, the electrolytic solution concerning this invention is explained concretely.

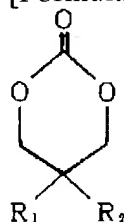
The nonaqueous electrolyte concerning nonaqueous electrolyte this invention for electric

double layer capacitors consists of the electrolyte solvent and electrolyte containing the annular carbonate expressed with the following type (I) or (II).

[0016] The annular carbonate expressed with an annular carbonate \*\*\*\* type (I) is explained.

[0017]

[Formula 5]



(I)

[0018] Among a formula, even if R<sub>1</sub> and R<sub>2</sub> are the same, they may differ from each other, and they are the alkyl group of carbon numbers 1-4, the unsaturated hydrocarbon radical of carbon numbers 2-4, or the aryl group of carbon numbers 6-12.

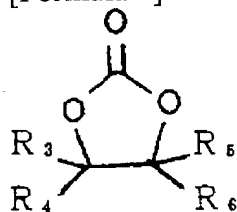
[0019] As the annular carbonate expressed with such a formula (I), Concretely, the 5 and 5-dimethyl -1, 3-dioxane-2-ON, 5, and 5-diethyl -1, 3-dioxane-2-ON, 5, and 5-divinyl -1, 3-dioxane-2-ON, the 5-vinyl-5-methyl -1, 3-dioxane-2-ON, the 5-ethyl-5-methyl -1, 3-dioxane-2-ON, etc. are mentioned.

[0020] The 5 R<sub>1</sub> and whose R<sub>2</sub> are CH<sub>3</sub> or C<sub>2</sub>H<sub>5</sub> among annular carbonates expressed with above-mentioned formula (I), 5-dimethyl -1, 3-dioxane-2-ON and 5, and 5-diethyl -1, and 3-dioxane-2-ON are desirable.

[0021] Next, the annular carbonate expressed with a formula (II) is explained.

[0022]

[Formula 6]



(II)

[0023] Among a formula, even if R<sub>3</sub>, R<sub>4</sub>, R<sub>5</sub>, and R<sub>6</sub> are the same, they may differ from each other, and they are the alkyl group of carbon numbers 1-4, or the aryl group of carbon numbers 6-12. As the annular carbonate expressed with such a formula (II), Concretely, it is [ - 4 5, and 5-trimethyl / -The 1, 3-dioxolane-2-ON, 4, and 4-diethyl -5 the 5-dimethyl -1, 3-dioxolane-2-ON, etc. are mentioned. ] 4, 4, 5, and 5-tetramethyl. - 1, 3-dioxolane-2-ON, 4-ethyl - 4, 5, and 5-trimethyl -1, 3-dioxolane-2-ON, 4

[0024] As an annular carbonate expressed with the above-mentioned formula (II), it is 4, 4, 5, and 5-tetramethyl [ R<sub>3</sub>-tetramethyl R<sub>6</sub> are CH<sub>3</sub> or C<sub>2</sub>H<sub>5</sub> ]. - 1, 3-dioxolane-2-ON, 4, 4 and 5, 5-tetraethyl -1, and 3-dioxolane-2-ON are desirable.

[0025] Without oxidizing, even if it excels in acid resistance and leaves it in air, the annular carbonate expressed with such a formula (I) and (II) is chemically stable, and it does not react with water by the usual state of preservation, or it does not react with reactant high material like a metal lithium. Furthermore, such an annular carbonate is physically safe, a pyrolysis is hard to be carried out, and it has the property of being hard

to receive electrochemical oxidation and reduction by fire retardancy.

[0026] Therefore, such an annular carbonate can be suitably used as a solvent for the electrolytic solutions, such as a capacitor, a cell, and electrochemical reaction. Moreover, it can use suitably also as medical drugs and agricultural chemicals, an acrylic-fiber processing agent, a high-molecular-compound solvent, and an organic middle raw material in addition to the electrolytic solution.

[0027] In electrolyte solvent this invention, the solvent which contains the annular carbonate expressed with the above-mentioned formula (I) or (II) as an electrolyte solvent is used. Even if such an electrolyte solvent is a mixed solvent of the annular carbonate expressed with the above-mentioned formula (I) even if it is the independent solvent of the annular carbonate expressed with the above-mentioned formula (I) or (II), and the annular carbonate expressed with the above-mentioned formula (II), it may be a mixed solvent of the annular carbonate expressed with the above-mentioned formula (I) and/or (II), and other solvents.

[0028] As other solvents, it is ethylene carbonate (1, 3-dioxolane-2-ON), Propylene carbonate (the 4-methyl -1, 3-dioxolane-2-ON), Butylene carbonate (4, the 5-dimethyl -1, 3-dioxolane-2-ON), Vinylene carbonate, 4-vinyl ethylene carbonate, 4, 5-divinyl ethylene carbonate, Annular carbonates, such as 4-methyl vinylene carbonate, dimethyl carbonate, Methylethyl carbonate, diethyl carbonate, methylpropyl carbonate, Chain-like carbonates, such as methyl isopropyl carbonate, gamma-butyrolactone, Cyclic ester, such as gamma-valerolactone, 3-methyl-gamma-butyrolactone, and 2-methyl-gamma-butyrolactone, Methyl formate, ethyl formate, methyl acetate, ethyl acetate, propyl acetate, Chain-like ester, such as methyl propionate, methyl butyrate, and valeric-acid methyl, 1,4-dioxane, 1, 3-dioxolane, a tetrahydrofuran, 2-methyl tetrahydrofuran, the 3-methyl -1, 3-dioxolane, Cyclic ether, such as the 2-methyl -1 and 3-dioxolane, 1, 2-dimethoxyethane, Phosphoric ester, such as \*\* sulfur compounds, such as the chain-like ether, such as 1, 2-diethoxy ethane, diethylether, wood ether, the methylethyl ether, and the dipropyl ether, and a sulfolane, and trimethyl phosphate, can be mentioned.

[0029] Moreover, the annular carbonate which has the halogen atom substitute alkyl indicated as an annular carbonate by JP,9-63644,A other than the annular carbonate of the above-mentioned instantiation can be used. As such an annular carbonate, mono-fluoro methyl ethylene carbonate, difluoromethyl ethylene carbonate, trifluoromethyl ethylene carbonate, etc. are mentioned.

[0030] One sort or two sorts or more can be mixed and used for these solvents. In this invention, when using the mixed solvent of the annular carbonate expressed with a formula (I) and/or (II), and other carbonates as an electrolyte solvent, a mixed solvent with the annular carbonate, the shape carbonate of an above chain, or annular carbonate expressed with a formula (I) and/or (II) is desirable. As for the annular carbonate expressed with a formula (I) and/or (II) with such an electrolyte solvent, it is desirable to be preferably contained in the amount more than 30 capacity % more than 10 capacity % to an electrolyte solvent total amount.

[0031] As the electrolyte contained in the nonaqueous electrolyte for electric double layer capacitors concerning electrolyte this invention, Concretely 4 fluoride way acid 4 butyl ammonium ( $C_4H_9$ ) ( $4NBF_4$ ), 4 fluoride way acid 4 ethylammonium ( $C_2H_5$ ) ( $4NBF_4$ ), 6 phosphorus-fluoride acid 4 butyl ammonium ( $C_4H_9$ ) ( $4NPF_6$ ), Ammonium salt, such as 6 phosphorus-fluoride acid 4 ethylammonium ( $C_2H_5$ ) ( $4NPF_6$ ), 4 fluoride way acid 4

butyl phosphonium (C<sub>4</sub>H<sub>9</sub>) (4PBF<sub>4</sub>), 4 fluoride way acid 4 ethyl phosphonium (C<sub>2</sub>H<sub>5</sub>) (4PBF<sub>4</sub>), The electrolyte used for the electrolytic solutions for usual electric double layer capacitors, such as phosphonium salt, such as 6 phosphorus-fluoride acid 4 butyl phosphonium (C<sub>4</sub>H<sub>9</sub>) (4PPF<sub>6</sub>) and 6 phosphorus-fluoride acid 4 ethyl phosphonium (C<sub>2</sub>H<sub>5</sub>) (4PPF<sub>6</sub>), is mentioned. These electrolytes can be used combining one sort or two sorts or more.

[0032] 4(C<sub>4</sub>H<sub>9</sub>) NBF<sub>4</sub> and 4(C<sub>2</sub>H<sub>5</sub>) NBF<sub>4</sub> are used preferably among these. As for such an electrolyte, it is desirable to usually contain 0.1-3 mols /in the amount of 0.5-1.5 mols/l. preferably 1. in the nonaqueous electrolyte for electric double layer capacitors.

[0033] Since the nonaqueous electrolyte for electric double layer capacitors concerning this invention contains the annular carbonate expressed with the above-mentioned formula (I) or (II), its withstand voltage is high and it is excellent in the charge-and-discharge cycle property. Moreover, the nonaqueous electrolyte concerning this invention has the high flash point, and it excels solvents, such as 1, 3-dioxolane and tetrahydrofuran, 1, and 2-diethoxy ethane, in safety. [ which are conventionally used for the electrolytic solution ]

[0034] For this reason, if the nonaqueous electrolyte for electric double layer capacitors concerning this invention is used, it is safe, withstand voltage is high, and the electric double layer capacitor excellent in the charge-and-discharge cycle property can be obtained.

[0035]

[Effect of the Invention] The nonaqueous electrolyte concerning this invention has high withstand voltage, and is excellent in safety and a charge-and-discharge cycle property.

[0036] If an electric double layer capacitor is formed using the nonaqueous electrolyte especially built over this invention, the high voltage can be generated, it can excel in a charge-and-discharge cycle property, and energy density can obtain a high electric double layer capacitor.

[0037]

[Example] Hereafter, although this invention is explained still more concretely based on an example, this invention is not limited at all by these examples.

[0038]

[Example 1] 4 fluoride way acid 4-ethylammonium (C<sub>2</sub>H<sub>5</sub>) (4NBF<sub>4</sub>) 2.71g (0.0125 mols) was dissolved in the mixed solvent which mixed the 5 and 5-dimethyl -1, and 3-dioxane-2-ON and propylene carbonate by the weight ratio 1:1, and the 25ml electrolytic solution was prepared (electrolytic concentration of 0.5 mols/l.).

[0039] Withstand voltage was measured about the obtained electrolytic solution.

The above-mentioned electrolytic solution was put into 3 pole type withstand voltage measurement cel which used the glassy carbon electrode for the withstand voltage operation pole and the counter electrode, and used the Ag/Ag<sup>+</sup> electrode for the reference pole, the sweep of the potential was carried out by 10 mV/sec with the potentio galvanostat, and oxidation reduction decomposition current made withstand voltage the range which did not flow more than 1microA on the basis of the Ag/Ag<sup>+</sup> electrode.

[0040] A result is shown in a table 1.

[0041]

[The example 1 of a comparison] In the example 1, the electrolytic solution was prepared and evaluated like the example 1 instead of the mixed solvent of the 5 and 5-dimethyl -1,

3-dioxane-2-ON, and propylene carbonate except having used propylene carbonate.

[0042] A result is shown in a table 1.

[0043]

[A table 1]

表 1

|       | 溶媒                                       | 耐電圧 (V) |      |
|-------|--|---------|------|
|       |  | 酸化電位    | 還元電位 |
| 実施例 1 | 5,5-ジメチル-1,3-ジオキサン-2-オン<br>+ プロピレンカーボネート | 3.1     | -3.2 |
| 比較例 1 | プロピレンカーボネート                              | 1.9     | -3.1 |

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[Translation done.]